

## REACTIVE HOT MELT ADHESIVE

## FIELD OF THE INVENTION

The invention relates to hot melt adhesives, in particular reactive hot melt adhesives having improved green strength.

## BACKGROUND OF THE INVENTION

Hot melt adhesives are solid at room temperature but, upon application of heat, melt to a liquid or fluid state in which form they are applied to a substrate. On cooling, the adhesive regains its solid form. The hard phase(s) formed upon cooling the adhesive imparts all of the cohesion (strength, toughness, creep and heat resistance) to the final adhesive. Curable hot melt adhesives, which are also applied in molten form, cool to solidify and subsequently cure by a chemical crosslinking reaction. An advantage of hot melt curable adhesives over traditional liquid curing adhesives is (1) their ability to provide "green strength" upon cooling prior to cure and (2) provide adhesives of very low crosslinking density and thus high levels of flexibility and toughness.

The majority of reactive hot melts are moisture-curing urethane adhesives. These adhesives consist primarily of isocyanate terminated polyurethane prepolymers that react with surface or ambient moisture in order to chain-extend, forming a new polyurethane polymer. Polyurethane prepolymers are conventionally obtained by reacting diols with diisocyanates. Pure diols are favored for use, instead of polyols with higher functionality, to avoid excessive branching that can lead to poor pot stability. Methylene bisphenyl diisocyanate (MDI) is favored over lower molecular weight isocyanates to minimize volatility. Cure is obtained through the diffusion of moisture from the atmosphere or the substrates into the adhesive, and subsequent reaction. The reaction of moisture with residual isocyanate forms carbamic acid. This acid is unstable, decomposing into an amine and carbon dioxide. The amine reacts rapidly with isocyanate to form a urea. The final adhesive product is a lightly crosslinked material held together primarily through hydrogen bonding, urea groups and urethane groups.

The prior art discloses that that the performance of reactive hot melt adhesives for most applications may be substantially improved by the incorporation of acrylic polymers into conventional polyurethane adhesives, in particular reactive hydroxy-containing and non-reactive acrylic copolymers. Improvement in green strength may be obtained by adding higher molecular weight polymers (reactive or not) and/or incorporating crystalline diols, most commonly polyester diols.

These prior art adhesives are extremely tough, with outstanding low temperature flexibility, heat and chemical resistance, and specific adhesion to polar substrates. Adhesion to a wide range of other substrates may be obtained through the addition of adhesion promoters such as silane coupling agents. Despite these advances in the art, there remains a need for improvements in reactive hot melt technology to expand the application of such adhesives and their effectiveness in such applications. The present invention addresses this need.

#### SUMMARY OF THE INVENTION

The invention provides moisture curable reactive hot melt adhesive compositions that have improved green strength.

One aspect of the invention is directed to a polyurethane hot melt adhesive composition comprising an isocyanate, from about 10 to about 60% of at least one substantially non-crystalline polyol, and from about 1 to about 30% of a functional acrylic polymer, wherein said adhesive composition comprises not more than about 10% of a substantially crystalline polyol. A preferred non-crystalline polyol is a polyether polyol. The at least one non-crystalline polyol may be mixture of non-crystalline polyols comprising from about 10 to about 60% of a polyether, up to about 40% of an aromatic polyester, up to about 40% of an aliphatic polyester, and up to about 40% of a polybutadiene. Optionally, the adhesive of the invention may further comprise a crystalline polyester and/or a non-functional acrylic. Preferred functional acrylics are hydroxyl functional acrylic polymers.

Another embodiment of the invention is directed to a method of improving the green strength of a polyurethane hot melt adhesive comprising adding from about 10 to about 60% of at least one substantially non-crystalline polyol to an adhesive composition which comprises from about 1 to about 30% of a functional acrylic polymer, and which comprises not more than about 10% of a substantially crystalline polyol.

Yet another embodiment of the invention is directed to a method for bonding materials together which comprises applying the reactive hot melt adhesive composition of the invention in a liquid form to a first substrate, bringing a second substrate in contact with the composition applied to the first substrate, and subjecting the applied composition to conditions which will allow the composition to cool and cure to an irreversible solid form, said conditions comprising moisture.

Still another aspect of the invention is directed to an article of manufacture comprising the adhesive of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The disclosures of all documents cited herein are incorporated in their entireties by reference.

All percents are percent by weight of the adhesive composition, unless otherwise stated.

It has now been discovered that high green strength reactive hot melt adhesives may be prepared using relatively low levels of reactive acrylic and, in addition, may be prepared without using crystalline polyester polyols. The adhesives of the invention have improved green strength and are resistant to hydrolysis under both alkaline and acidic conditions.

The moisture curable, hot melt polyurethane adhesives of the invention may be prepared through the reaction of a mixture of substantially non-crystalline polyols with an isocyanate-containing compound at a temperature of from about 250°F to about 275°F.

The adhesives of the invention comprise an isocyanate, MDI being preferred, from

about 10 to about 60% of at least one non-crystalline polyol, and from about 1 to about 30% of a functional acrylic.

A non-crystalline polyol, as this term is understood in the art, refers to a liquid or amorphous polyol.

Non-crystalline polyol mixtures which may be used to practice the invention generally comprise from about 10 to about 60 percent of a substantially non-crystalline polyether, from about 0 to about 40 percent of an aromatic polyester, from about 0 to about 40 percent of a substantially non-crystalline aliphatic polyester, from about 0 to about 40 percent of a polybutadiene.

If desired, from about 0 to about 50 percent of functional acrylic and/or from about 0 to about 10 percent crystalline polyester may be added to the adhesive compositions of the invention.

The reactive hot melt compositions of the invention are useful for bonding articles composed of a wide variety of substrates (materials), including but not limited to wood, metal, glass and textiles. The adhesives of the invention are resistant to hydrolysis under alkaline or acid conditions, and are resistant to reactions of hydroxy- and carboxy-containing products, such as fatty acids, tall oil, ethylene glycol and propylene glycol. As such, these adhesives find particular use in applications such as use in water towers, for bonding to exterior surfaces, bonding to wood with high levels of pitch and e.g., in marine and automotive applications. Other non-limiting uses include textile bonding applications (carpet and clothing), use in the manufacture of footwear (shoes), use as a glazing/backbedding compound in the manufacture of windows, use in the manufacture of doors including entry doors, garage doors and the like, use in the manufacture of architectural panels, use in bonding components on the exterior of vehicles, and the like.

The urethane prepolymers that can be used to prepare the adhesives of the invention are those conventionally used in the production of polyurethane hot melt adhesive compositions. Any suitable compound, which contains two or more isocyanate groups, may

be used for preparing the urethane prepolymers. Typically from about 2 to about 25 parts by weight of an isocyanate is used.

Organic polyisocyanates, which may be used to practice the invention, include alkylene diisocyanates, cycloalkylene diisocyanates, aromatic diisocyanates and aliphatic-aromatic diisocyanates. Specific examples of suitable isocyanate-containing compounds include, but are not limited to, ethylene diisocyanate, ethyldene diisocyanate, propylene diisocyanate, butylene diisocyanate, trimethylene diisocyanate, hexamethylene diisocyanate, toluene diisocyanate, cyclopentylene-1, 3-diisocyanate, cyclo-hexylene-1,4-diisocyanate, cyclohexylene-1,2-diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,2-diphenylpropane-4,4'-diisocyanate, xylylene diisocyanate, 1,4-naphthylene diisocyanate, 1,5-naphthylene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, diphenyl-4,4'-diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulphone-4,4'-diisocyanate, 2,4-tolylene diisocyanate, dichlorohexa-methylene diisocyanate, furfurylidene diisocyanate, 1-chlorobenzene-2,4-diisocyanate, 4,4',4"-triisocyanatotriphenylmethane, 1,3,5-triisocyanato-benzene, 2,4,6-triisocyanato-toluene, 4,4'-dimethyldiphenyl-methane-2,2',5,5-tetratetraisocyanate, and the like. While such compounds are commercially available, methods for synthesizing such compounds are well known in the art. Preferred isocyanate-containing compounds are methylenebisphenyldiisocyanate (MDI), isophoronediisocyanate (IPDI) and toluene diisocyanate (TDI).

Most commonly, the prepolymer is prepared by the polymerization of a polyisocyanate with a polyol, most preferably the polymerization of a diisocyanate with a diol. The polyols used include polyhydroxy ethers (substituted or unsubstituted polyalkylene ether glycols or polyhydroxy polyalkylene ethers), polyhydroxy polyesters, the ethylene or propylene oxide adducts of polyols and the monosubstituted esters of glycerol, as well as mixtures thereof. The polyol is typically used in an amount of between about 10 to about 70 parts by weight.

Examples of polyether polyols include a linear and/or branched polyether having plural numbers of ether bondings and at least two hydroxyl groups, and contain substantially no

functional group other than the hydroxyl groups. Examples of the polyether polyol may include polyoxyalkylene polyol such as polyethylene glycol, polypropylene glycol, polybutylene glycol and the like. Further, a homopolymer and a copolymer of the polyoxyalkylene polyols may also be employed. Particularly preferable copolymers of the polyoxyalkylene polyols may include an adduct at least one compound selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, 2-ethylhexanediol-1,3, glycerin, 1,2,6-hexane triol, trimethylol propane, trimethylol ethane, tris(hydroxyphenyl)propane, triethanolamine, triisopropanolamine, ethylenediamine and ethanolamine; with at least one compound selected from the group consisting of ethylene oxide, propylene oxide and butylene oxide.

Polyester polyols are formed from the condensation of one or more polyhydric alcohols having from 2 to 15 carbon atoms with one or more polycarboxylic acids having from 2 to 14 carbon atoms. Examples of suitable polyhydric alcohols include ethylene glycol, propylene glycol such as 1,2-propylene glycol and 1,3-propylene glycol, glycerol, pentaerythritol, trimethylolpropane, 1,4,6-octanetriol, butanediol, pentanediol, hexanediol, dodecanediol, octanediol, chloropantanediol, glycerol monallyl ether, glycerol monoethyl ether, diethylene glycol, 2-ethylhexanediol-1,4, cyclohexanediol-1,4, 1,2,6-hexanetriol, 1,3,5-hexanetriol, 1,3-bis-(2-hydroxyethoxy)propane and the like. Examples of polycarboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, maleic acid, dodecylmaleic acid, octadecenylmaleic acid, fumaric acid,aconitic acid, trimellitic acid, tricarballylic acid, 3,3'-thiodipropionic acid, succinic acid, adipic acid, malonic acid, glutaric acid, pimelic acid, sebacic acid, cyclohexane-1,2-dicarboxylic acid, 1,4-cyclohexadiene-1,2-dicarboxylic acid, 3-methyl-3,5-cyclohexadiene-1,2-dicarboxylic acid and the corresponding acid anhydrides, acid chlorides and acid esters such as phthalic anhydride, phthaloyl chloride and the dimethyl ester of phthalic acid. Preferred polycarboxylic acids are the aliphatic and cycloaliphatic dicarboxylic acids containing no more than 14 carbon atoms and the aromatic dicarboxylic acids containing no more than 14 atoms.

Commercially available polyols which may be used in the practice of the invention include polyethers such as ARCOL PPG 2025 (Bayer), PolyG 20-56 (Arch) and Pluracol P-2010 (BASF), polyesters such as Dynacol 7360 (Creanova), Fomrez 66-32 (Crompton) and Rucoflex S-105-30 (Bayer) and polybutadiene such as PolyBD R-45HTLO (Elf Atochem).

In addition, the urethane prepolymers may be prepared by the reaction of a polyisocyanate with a polyamino or a polymercapto-containing compound such as diamino polypropylene glycol or diamino polyethylene glycol or polythioethers such as the condensation products of thiodiglycol either alone or in combination with other glycols such as ethylene glycol, 1,2-propylene glycol or with other polyhydroxy compounds disclosed above. In accordance with one embodiment of the invention, the hydroxyl containing acrylic polymer may function as the polyol component, in which case, no additional polyol need be added to the reaction.

Further, small amounts of low molecular weight dihydroxy, diamino, or amino hydroxy compounds may be used such as saturated and unsaturated glycols, e.g., ethylene glycol or condensates thereof such as diethylene glycol, triethylene glycol, and the like; ethylene diamine, hexamethylene diamine and the like; ethanolamine, propanolamine, N-methyldiethanolamine and the like.

Virtually any ethylenically unsaturated monomer containing a functionality greater than one may be utilized in the compositions of the present invention. Functional monomers include, without limitation acid, hydroxy, amine, isocyanate, and thio functional monomers. Hydroxyl functionality is preferred and is described in detail herein.

Most commonly employed are hydroxyl substituted C<sub>1</sub> to C<sub>12</sub> esters of acrylic and methacrylic acids including, but not limited to hydroxyl substituted methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, isobutyl acrylate, n-propyl or iso-propyl acrylate or the corresponding methacrylates. Mixtures of compatible (meth)acrylate monomers may also be used. Additional monomers that may be used include the hydroxyl substituted vinyl

esters (vinyl acetate and vinyl propionate), vinyl ethers, fumarates, maleates, styrene, acrylonitrile, etc. as well as comonomers thereof.

These monomers may be blended with other copolymerizable comonomers as formulated so as to have a wide range of Tg values, as between about -48° C and 105° C, preferably 15° C to 85° C. Suitable comonomers include the C<sub>1</sub> to C<sub>12</sub> esters of acrylic and methacrylic acids including, but not limited to methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-propyl or iso-propyl acrylate or the corresponding methacrylates. Mixtures of compatible (meth)acrylate monomers may also be used.

Additional monomers that may be used include the vinyl esters (vinyl acetate and vinyl propionate), vinyl ethers, fumarates, maleates, styrene, acrylonitrile, ethylene, etc. as well as comonomers thereof. The hydroxyl containing monomers may be the same or different from the monomers used in the remainder of the acrylic polymerization. The particular monomers selected will depend, in large part, upon the end use for which the adhesives are intended. Thus, adhesives to be used in pressure sensitive applications or in applications wherein adhesion to metal is required will be selected to obtain a lower Tg polymer than may be desired in non-pressure sensitive applications or those involving more easily bonded substrates.

When the adhesive is to be prepared utilizing monomeric materials, the respective monomers may be added to the polyols and polymerized therein prior to formation of the prepolymer or may be added to the already formed prepolymer and the acrylic polymerization subsequently performed. In the case of polyamino or polymercapto containing prepolymers, in-situ vinylic polymerization must be performed only in the pre-formed prepolymer.

The hydroxyl containing ethylenically unsaturated monomer is polymerized using conventional free radical polymerization procedures to a relatively low molecular weight. For purposes of clarification, use of the term "low molecular weight" means number average molecular weights in the range of approximately 2,000 to 50,000, preferred for use are monomers having an average molecular weight in the range of from about 5,000 to about

30,000. Molecular weight distribution is characterized by Gel Permeation Chromatography using a PL Gel, Mixed 10 micron column, a Shimadzu Model RID 6A Detector with a tetrahydrofuran carrier solvent at a flow rate of 1 milliliter per minute. The low molecular weight is obtained by careful monitoring and controlling the reaction conditions and, generally, by carrying out the reaction in the presence of a chain transfer agent such as dodecyl mercaptan. Subsequent to the polymerization of the ethylenically unsaturated monomer(s), the polyisocyanate and any additional ingredients required for the urethane prepolymer forming reaction are added and that reaction is carried out using conventional condensation polymerization procedures. In this manner, the resultant isocyanate terminated urethane prepolymer forms the reactive curing hot melt adhesive described above which contains about 2 to about 30 % of the low molecular weight hydroxyl containing polymer.

It is also possible to polymerize the low molecular weight polymer in the presence of the already formed isocyanate terminated urethane prepolymer. This method has the drawback of subjecting the prepolymer to unnecessary heating during the acrylic polymerization, heating that might result in branching, viscosity increase, depletion of needed isocyanate groups and possible gellation. Although these disadvantages are subject to control, more stringent control of conditions are required as compared to polymerization in the non-isocyanate functional urethane components. When the reaction is run in the polyol or other non-isocyanate containing component, there is also the advantage of lower reaction viscosities and reduced exposure to isocyanate vapors because of the lesser amount of heating required.

Optionally, the hydroxyl containing functionality may be introduced into the adhesive in the form of pre-polymerized low molecular weight hydroxyl containing polymers. In the latter case, typical polymers include hydroxyl substituted butyl acrylate, hydroxylated butyl acrylate/methyl methacrylate copolymers, hydroxylated ethyl acrylate/methyl methacrylate copolymers, and the like. Preferred polymers have a number average molecular weight of 5,000 to 30,000 and a hydroxyl number of 4 to 30. If used in the form of low molecular weight

polymers, the polymers may be blended with the polyol prior to reaction thereof with the isocyanate or they may be added directly to the isocyanate terminated prepolymer.

While the adhesives may be used directly as described above, if desired the adhesives of the present invention may also be formulated with conventional additives which are compatible with the composition. Such additives include plasticizers, compatible tackifiers, curing catalysts, dissociation catalysts, fillers, anti-oxidants, pigments, adhesion promoters, stabilizers and the like. Conventional additives that are compatible with a composition according to this invention may simply be determined by combining a potential additive with the composition and determining if they are compatible. An additive is compatible if it is homogenous within the product. Non-limited examples of suitable additives include, without limitation, rosin, rosin derivatives, rosin ester, aliphatic hydrocarbons, aromatic hydrocarbons aromatically modified aliphatic hydrocarbons, terpenes, terpene phenol, modified terpene, high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorous-containing phenol, terpene oligomers, DMDEE, paraffin waxes, microcrystalline waxes and hydrogenated castor oil.

The reactive hot melt adhesives of the invention may also contain flame retardant components. Fire retardant additives known in the art for imparting flame resistance to polyurethane compositions may be added. Such compounds include inorganic compounds such as a boron compound, aluminum hydroxide, antimony trioxide and the like, and other halogen compounds including halogen-containing phosphate compounds such as tris(chloroethyl)phosphate, tris(2,3-dichloropropyl)-phosphate, and the like. These and other flame retarding compositions are described in U.S. Patent Nos. 3,773,695 4,266,042, 4,585,806, 4,587,273 and 4,849,467, and European Patent No. 0 587 942. In a preferred embodiment, ethylenebistetrabromophthalimide and/or tris(2,3-dibromopropyl)-isocyanurate is added as a prime flame retardant component. The ethylenebistetrabromophthalimide and/or tris(2,3-dibromopropyl)isocyanurate may be used with or without other flame retardants. The composition may further comprise a chlorinated paraffin and/or an aryl phosphate ester as a

further flame retardant component. The optional chlorinated paraffin imparts flame retardancy as well as performing as a viscosity modifier. The aryl phosphate ester further imparts improved adhesion to the substrates. The flame retardant polyurethane-based reactive hot melt adhesives when used in the practice of the invention gives excellent flame retardancy while maintaining the targeted properties of the base polymer, such as good green strength, controlled setting speed and good thermal stability at elevated temperatures.

The invention also provides a method for bonding articles together which comprises applying the reactive hot melt adhesive composition of the invention in a liquid melt form to a first article, bringing a second article in contact with the composition applied to the first article, and subjecting the applied composition to conditions which will allow the composition to cool and cure to a composition having an irreversible solid form, said conditions comprising moisture. The composition is typically distributed and stored in its solid form, and is stored in the absence of moisture. When the composition is ready for use, the solid is heated and melted prior to application. Thus, this invention includes reactive polyurethane hot melt adhesive compositions in both its solid form, as it is typically to be stored and distributed, and its liquid form, after it has been melted, just prior to its application.

After application, to adhere articles together, the reactive hot melt adhesive composition is subjected to conditions that will allow it to solidify and cure to a composition that has an irreversible solid form. Solidification (setting) occurs when the liquid melt is subjected to room temperature. Curing, i.e. chain extending, to a composition that has an irreversible solid form, takes place in the presence of ambient moisture.

As used herein, "irreversible solid form" means a solid form comprising polyurethane polymers extended from the aforementioned polyurethane prepolymers. The composition having the irreversible solid form typically can withstand temperatures of up to 150°C. Using a flame retardant the thermal stability of the irreversible solid can be improved.

The invention is further illustrated by the following non-limiting examples.

## EXAMPLES

In the Examples that follow, the following tests were used to determine viscosity and dynamic peel rate.

### Viscosity:

Brookfield Viscometer with Thermosel heating unit, spindle 27

### Dynamic Peel:

A 6 mil film of the adhesive was applied to a glass plate, preheated at 120°C. A strip of vinyl (16mm wide, 7 mil thick) with a hole punched near one end was applied over the adhesive. The plate is inverted and, at several temperature intervals, a 103g weight was applied to the hole in the vinyl for 10-60 seconds. The peel rate at these intervals was calculated.

### Example

Reactive hot melt adhesives having the formulations shown in Table 1 (% by weight) were prepared. All the polyols and acrylic polymers (reactive or not) were added to melt and mix under vacuum until homogeneous and free of moisture. Then MDI was added and polymerization allowed to proceed with mixing under vacuum until reaction is complete. The resulting pre-polymer was then placed into a container under a dry nitrogen headspace to prevent exposure to moisture.

Table 1

Material	Sample A	Sample B	Sample C
PolyG 20-56	36.25	35.1	19.8
PolyG 20-28	---	---	19.8
ELVACITE 2901	10.35	6.15	---
ELVACITE 2016	19.45	---	28.2
ELVACITE 2967	19.45	6.15	---
ELVACITE 2013	---	33.85	---
DYNACOLL 7360	---	---	19.80
MODAFLOW	0.25	0.15	0.9
TiO <sub>2</sub> Dispersion GRK 814	---	3.50	---
MONDUR M	14.25	15.10	11.3
DMDEE	---	---	0.2

PolyG 20-56 (a 2000 MW polyether polyol - available from Arch)

PolyG 20-28 (a 4000 MW polyether polyol available from Arch)

Dynacoll 7360 (a 3750 MW hexanediol adipate available from Creanova)

ELVACITE 2901 (an 82°C Tg/50,000 Mw acrylic, OH-functional - available from Ineos)

ELVACITE 2016 ( a 55°C Tg/65,000 Mw acrylic - available from Ineos)

ELVACITE 2967 ( a 17°C Tg/20,000 Mw acrylic, OH-functional - available from Ineos)

ELVACITE 2013 ( a 80°C Tg/50,000 Mw acrylic - available from Ineos)

MODAFLOW (an acrylic defoamer available from Solutia)

TiO<sub>2</sub> Dispersion GRK 814 (45% TiO<sub>2</sub> in PolyG 20-56 - available from Spectrum Dispersions)

MONDUR M (4, 4' MDI available from Bayer)

DMDEE (2,2' dimorpholinodiethyl ether - available from Rhelin Chemie)

Samples A and B were formulated using less than 30% functional acrylic and no crystalline polyester polyol. Sample A contained 29.8% functional acrylic and Sample B contained 12.3% functional acrylic. Comparative Sample C is a conventional reactive hot melt containing a crystalline aliphatic polyester polyol. The adhesive properties of Samples A, B and C were compared. Results are shown in Table 2.

Table 2

	Sample A	Sample B	Sample C
Viscosity	9850 (275°C)	9250 (275°C)	12,800 (250°C)
Viscosity growth (%/hour)	2.8%	4.3%	0.8%
Dynamic peel (35°C) (45°C)	8 mm/min 75 mm/min	0 mm/min 11 mm/min	30 mm/min 135 mm/min
%NCO	3.0%	3.0%	1.9%

The functional acrylic-containing Samples A and B possessed better set strength than comparative Sample C, as measured by dynamic peel. The Strength of Sample B is substantially better than Sample A, even though the functional acrylic level is lower by more than 50%. This data shows that high green strength reactive hot melts can be prepared without crystalline aliphatic polyester polyols using functional acrylics at levels below 30 weight %.

Many modifications and variations of this invention can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. The specific embodiments described herein are offered by way of example only, and the invention is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled.